CALIBRATION OF MASS SPECTROMETER FOR ISOTOPIC MEASUREMENTS OF CO_2 AND H_2

PROCEDURE ID: YMP-LBNL-TIP/TT11.0 | REV. 1, MOD. 0 | EFFECTIVE 06/08/01

1. PURPOSE

This Technical Implementing Procedure (TIP) describes a method to calibrate a mass spectrometer for isotopic measurements of CO_2 and H_2 for the Yucca Mountain Site Characterization Project (YMP) at Lawrence Berkeley National Laboratory (LBNL).

2. SCOPE

This procedure covers specific requirements for calibrating and checking the calibration of standard gases used for measuring the stable isotopic compositions of H_2 and CO_2 gas samples with the VG Isotech Prism Series II Isotope Ratio Mass Spectrometer (Prism) of the Center for Isotope Geochemistry (CIG). The Prism is located in Building 70A, Room 4425 at LBNL. This document does not cover the use of process standards for calibration of the different analytical procedures used for measurements of samples (these are included in the TIPs for the individual procedures).

This procedure shall be used by all LBNL personnel (or contractor personnel following LBNL procedures) whenever they are required to calibrate or check the calibration of the Prism. Prior to conducting work described in Section 3 of this procedure, personnel performing calibrations, other than verifications or at-each-use calibrations, require training to this procedure. All technical activities including data collected using this procedure and any equipment calibrations or recalibrations that may be required shall be in accordance with this TIP and Administrative Procedure (AP)-12.1Q, *Control of Measuring and Test Equipment and Calibration Standards.*

If this procedure cannot be implemented as written, YMP-LBNL personnel shall notify the responsible Principal Investigator (PI) or designee. If it is determined that a portion of the work cannot be accomplished as described in this TIP, or would produce undesirable results, that portion of the work shall be stopped and not resumed until the procedure is modified per YMP-LBNL-QIP-5.2, *Preparing Quality & Technical Implementing Procedures.*

If the responsible PI or designee determines that a modification or a revision to the TIP would cause an unreasonable delay in proceeding with the task, then an expedited change to the procedure, including documentation of deviation from

the approved procedure, can be made according to the YMP-LBNL-QIP-5.2. Such changes are subject to review, usually after the task has proceeded, and thus work performed under TIPs with expedited changes is done at risk of future invalidation.

Employees may use copies of this procedure printed from the controlled document electronic file; however, employees are responsible for assuring that the correct revision of this procedure is used. When this procedure becomes obsolete or superseded, it must be destroyed or marked "superseded" to ensure that this document is not used to perform work.

3. PROCEDURE

3.1 Principle

Precise analyses of the stable isotopic compositions of CO_2 ($\delta^{13}C$ and $\delta^{18}O$ values) and H_2 (δD values) on dual inlet isotope ratio mass spectrometers, such as the Prism, are made by comparing the ratios of beam intensities for different isotopes in an unknown gas to those in a standard gas with a known isotopic composition. This corrects for unavoidable shifts in the isotopic composition of the samples that occur during the analysis of the gas with the mass spectrometer. Therefore, it is essential that the values of the standard gas be precisely known. When it is necessary to determine the isotopic composition of a new standard gas or periodically check that the composition of an existing standard gas is correct, we use standards with known isotopic ratios (National Institute of Standards and Technology [NIST] standards).

3.2 Materials/Equipment Required

- VG Isotech Prism Series II Isotope Ratio Mass Spectrometer (Prism)
- A tank of high purity H_2 gas (99.95%)
- Water standards (NIST standards VSMOW, GISP and SLAP)
- 2 g of calcite or aragonite with carbon and oxygen isotope ratios in the range of VPDB (within ±20‰ is sufficient)
- Ortho-phosphoric acid (H_3PO_4)
- Glass vacuum line with flow-through traps (Attachment 1)
- Two-legged glass reaction vessel (Attachment 2)
- Glass beads

- Dewars
- Liquid N_2 (LN)
- Methanol
- Thermometer capable of measuring between 0 and –100°C
- 1 liter tank for storing working standard gas with a valve at one end
- Gas standards (NIST standards CO_2-Heavy, CO_2-Light and CO_2-Biogenic) for calibrating CO_2 working standard gas

3.3 Calibration of New Standard Gas

3.3.1 All data generated as a result of this activity are entered into the Prism logbook (kept in Room 4425 of Building 70A at LBNL). Applicable elements of the Prism logbook shall be copied and attached into the scientific notebook in accordance with AP-SIII.1Q, *Scientific Notebooks.*

3.3.2 Description of equipment, retrievability status and calibration information shall be documented in accordance with AP-12.1Q, *Control of Measuring and Test Equipment and Calibration Standards* and forwarded to the M&TE Coordinator at LBNL.

3.3.3 Before loading the new standard gas into the standard gas reservoirs (1-liter tanks attached to the manifold beneath the multiport on the Prism), expand an aliquot of the old standard gas into the standard gas bellows of the Prism. To do this, evacuate the inlet by opening the low vacuum valve (LV) and open all the valves in the inlet. Also flip up the toggle switch between the standard manifold and the inlet. When the reading on Pirani gauge 2 has dropped to <1e-2 mbar, switch to high vacuum by closing LV and opening HV. After 1-2 minutes, close the valves RP and RI and open the manual valve on the standard gas tank. Wait approximately one minute and then close the valve on the standard gas tank and open RI, allowing the standard gas in the standard manifold to expand into the standard gas bellows. **Make sure the standard bellows are fully expanded** (in the 0 position). After the standard gas has had a chance to equilibrate, close RI and remove the standard tank from the standard manifold.

3.3.4 Attach the standard gas tank to the vacuum line (Attachment 1). Evacuate the standard tank by opening the valve at the top of the tank and the inlet valve of the sample port to which the tank is attached.

3.3.4.1 For hydrogen, attach a tank of high purity (>99.95%) H_2 gas to another port on the vacuum line and pump out the air in the connection to the vacuum line by opening the valve on the sample port. Isolate the vacuum line from the vacuum pump by closing all valves leading to the pump. Open the valve on the gas supply and expand approximately 1 atmosphere pressure of gas into the standard tank. Close the valves on the standard gas tank and the sample port and remove the tank from the vacuum line.

3.3.4.2 For carbon dioxide, produce CO_2 by dissolving 2 g of calcite or aragonite in phosphoric acid using the following steps:

3.3.4.2.1 Load 4 aliquots of approximately 0.5 g each of the carbonate into one side of the bottom section of a two-legged reaction vessel (Attachment 2). Load approximately 5 ml of ortho-phosphoric acid into the other leg. Seal the reaction vessels.

3.3.4.2.2 Attach the reaction vessels to the vacuum line. Slowly (to avoid sucking the carbonate powder into the vacuum line), open the valves on the reaction vessels to pump away the air in the vessels. After ~1 hour, close the valves on the vacuum line ports and on the top of the reaction vessels and remove the reaction vessels from the vacuum line.

3.3.4.2.3 Tip the reaction vessels to allow the ortho-phosphoric acid to drain into the leg with the carbonate powder. Let the samples react overnight.

3.3.4.2.4 Attach the reaction vessels to the vacuum line. Pump out the section between the reaction vessels and the vacuum line by opening the valves on the ports. Prepare methanol slushes for the two flow-through traps on the extraction line by slowly adding liquid

N_2 (LN) to a dewar containing methanol until the desired temperature is reached. The slush for flow-through trap 1 (containing glass beads) shall be maintained between -80 and -90°C. The second slush will be used intermittently on flow-through trap 2 and shall be kept between -60 and -70°C.

3.3.4.2.5 Place the colder slush on trap 1 and a dewar with LN on trap 2 of the vacuum line. Connect the 1-liter flask for the CO_2 working standard to one of the ports on the right side of the vacuum line and evacuate the flask. Immerse the bottom of the flask in a dewar filled with LN.

3.3.4.2.6 Close the valves above the left manifold and between flow-through trap 1 and flow-through trap 2. **Slowly** (to avoid rush of gas which can cause glass beads to break line) open the valve at the top of the first reaction vessel to allow the CO_2 produced by the reaction of the carbonate and the ortho-phosphoric acid to expand into the left manifold and the first trap. After approximately 1 minute, close the valve between flow-through trap 2 and the manometer volume and open the valve between the two flow-through traps. The pressure reading on thermocouple gauge 1 should drop as the CO_2 condenses into flow-through trap 2 (with LN). When the pressure reading on the thermocouple gauge stabilizes, record the amount of amount of non-condensable gases in the laboratory log book and pump away the non-condensable gases by opening the valve between flow-through trap 2 and the transducer volume and the valve between the right sample manifold and the vacuum pump.

3.3.4.2.7 When the readings on the thermocouple gauges have dropped to <10 millitorr above background, isolate the volume between flow-through trap 2 and the right manifold by closing the valves between the two flow-through traps and at the top of the right manifold. Replace the dewar with LN on flow-through trap 2 with the -60°C methanol slush. Open the valves

leading to the 1-liter flask, allowing the CO_2 in trap 2 to freeze into the flask. When the reading on thermocouple gauge 2 has stabilized, pump out any remaining non-condensable gas by opening the valve at the top of the right manifold. When the transducer reading has dropped to background, close the valve at the top of the 1-liter flask and remove the slush from the second flow-through trap and allow it to return to room temperature in order to pump away any water that may be in this trap.

3.3.4.2.8 Repeat steps 3.3.4.2.6 and 3.3.4.2.7 for the remaining 3 reaction vessels. When the CO_2 in all 4 reaction vessels has been transferred into the 1-liter flask, close the valve at the top of the flask, remove the dewar with LN and detach the flask from the vacuum line.

3.3.5 Re-attach the standard gas tank to the standard manifold on the Prism and pump out the air in the manifold by closing RF and then opening LV and RI (and the toggle switch if it was closed). When the reading on Pirani gauge 2 has dropped to <1e-2 mbar, switch to high vacuum by closing LV and opening HV.

3.3.6 Expand an aliquot of the new standard gas into the sample bellows of the Prism. To do this, first close the toggle switch and open the valve at the top of the standard gas tank. After about 1 minute, close HV and SI (if it is open), open SP, SF, SV and SM, and then open the toggle switch. **Make sure the sample bellows are fully expanded** (in the 0 position). After the new standard gas has had a chance to equilibrate, close RI and SP.

3.3.7 Analyze the isotopic composition of the new standard gas using the following method:

3.3.7.1 Adjust the sizes of beam 1 (mass 2 for H_2 and mass 44 for CO_2) for the reference bellows (with the old standard gas) and the sample bellows (with the new standard gas) to the same value (usually between 5e-9 and 8e-9 amps).

3.3.7.2 Under the "Analysis" menu for the operating software, choose the "DAPC Run…" option. Choose the appropriate File name ("HD" for hydrogen and "CO2" for carbon dioxide), enter the sample name and press "Run".

3.3.7.3 After analyzing the sample twice (at least), record the results in the Prism logbook. Enter the average value in the appropriate gas file (found in the "DAPC Edit…" window under the "Analysis" menu).

3.3.8 To check the calibration of the new standard gas, analyze in duplicate (at least) the isotopic compositions of the following Standard Reference Materials (SRMs) obtained from the NIST in Gaithersburg, MD (to place orders phone (301) 975-6776):

For H_2

- RM 8535 (VSMOW) for δD
- RM 8536 (GISP) for δD
- RM 8537 (SLAP) for δD

For CO_2

- RM 8562 CO_2-Heavy (Paleomarine Origin)
- RM 8563 CO_2-Light (Petrochemical Origin)
- RM 8564 CO_2-Biogenic (Modern Biomass Origin)

Record the run data in the Prism logbook and copies in the appropriate YMP Scientific Notebook(s).

3.3.9 If any discrepancies exist between the accepted and measured values for the NIST standards (they should be less than 2‰ off for H_2 and 0.2‰ off for CO_2), adjust the value of the working standard to give the correct values. For H_2, do this by subtracting the value measured for VSMOW from the value of the working standard. For CO_2,

subtract the y-intercept value for a best-fit line through the data for all 3 NIST standards (for both delta 45 and delta 46).

3.3.10 On a yearly basis or at any time when it is suspected that the isotopic composition of the working standards may have shifted (e.g., when the values of process standards included in sets of samples run on the mass spectrometer consistently differ from their accepted isotopic compositions by 1‰), the calibration of the standard gas shall be checked by repeating section 3.3.8.

3.3.11 Documentation

The following information shall be documented in the scientific notebook or on the M&TE Calibration Documentation Form (Attachment 3):

- The unique identifier of the mass spectrometer
- Date and time calibrated
- Calibration data, and results of the calibration and statement of acceptability
- Re-calibration due date or calibration interval / frequency
- Procedure (including revision level) used to calibrate the M&TE
- Identification of and traceability to the calibration standards used for the calibration
- As-found condition of the M&TE, as appropriate
- Specified range and tolerances and whether the M&TE met those tolerances
- Person(s) performing calibrations
- Reference to actions taken with out-of-calibration or non conforming M&TE, including evaluation results, as appropriate.

3.3.12 Calibration Tag

If the calibration results are acceptable, affix a calibration tag to the mass spectrometer. The tag shall state the M&TE unique identifier, date and name of the person who performed the calibration, next calibration date.

3.3.13 Control of Out-of-Tolerance Conditions

If the equipment is found to be out-of tolerance, affix an Out Of Calibration tag, giving the following information:

- Description and unique identifier of the M&TE
- Reason for applying the tag
- Dated signature of the person tagging the M&TE

Document the out-of-calibration condition on the Out Of Calibration Report required by AP-12.1Q and evaluate the impact to data collection, process monitored, or items evaluated. If it is determined that there is an impact, a Nonconformance report shall be initiated in accordance with AP-15.2Q.

4. RECORDS

4.1 Lifetime

Records generated as a result of this TIP are entries in the Prism logbook. Applicable elements of this logbook are entries in applicable scientific notebooks or attachments to such notebooks.

4.2 Non-Permanent

None

4.3 Controlled Documents

This Technical Implementing Procedure

4.4 Records Center Documents

Records associated with this procedure shall be submitted to the Records Coordinator of LBNL for transmittal to the Records Processing Center (RPC) in accordance with AP-17.1Q, *Record Source Responsibility for Inclusionary Records.*

5. RESPONSIBILITIES

5.1 The **Principal Investigator (PI)** or designee is responsible for assuring full compliance with this procedure and for providing training thereof. The PI

or designee is also responsible for overseeing and coordinating the preparation, review, distribution, revision, and rescission of the TIP.

5.5 Staff Members are responsible for following this procedure and turning over related documentation to the Records Coordinator for submittal to the RPC in accordance with AP-17.1Q. Related data shall be turned over to the Technical Data Coordinator for entry into the YMP Technical Data Management System (TDMS) in accordance with AP-SIII.3Q, *Submittal and Incorporation of Data to the Technical Data Management System.*

6. ACRONYMS AND DEFINITIONS

6.1 Acronyms

CIG Center for Isotope Geochemistry

LBNL Lawrence Berkeley National Laboratory

NIST National Institute of Standards and Technology

PI Principal Investigator

QIP Quality Implementing Procedure

RPC Records Processing Center

TDMS Technical Data Management System

TIP Technical Implementing Procedure

YMP Yucca Mountain Site Characterization Project

6.2 Definitions

Prism: VG Isotech Prism Series II Isotope Ratio Mass Spectrometer in Room 4425 of building 70A at LBNL.

Staff Member: Any scientist, engineer, research or technical associate, technician, or student research assistant performing quality-affecting work for YMP-LBNL.

Technical Implementing Procedure: Each TIP describes YMP-LBNL technical tasks that (1) are repetitive, and (2) are standardized.

7. REFERENCES

AP-17.1Q, *Record Source Responsibility for Inclusionary Records.*

AP-SIII.1Q, *Scientific Notebooks*

AP-SIII.3Q, *Submittal and Incorporation of Data to the Technical Data Management System*

AP-12.1Q, *Control of Measuring and Test Equipment and Calibration Standards*

YMP-LBNL-QIP-5.2, *Preparing Development Plans & Quality/Technical Implementing Procedures*

8. ATTACHMENTS

Attachment 1: Schematic diagram of glass vacuum line

Attachment 2: Schematic diagram of two-legged reaction vessel.

Attachment 3: Measuring and Test Equipment (M&TE) Calibration Documentation Form

9. REVISION HISTORY

09/30/98 – Revision 0, Modification 0:

This is the initial issue of this procedure. It is a derivative of a scientific process/methodology presented in scientific notebook YMP-LBNL-YWT-MC-1.

06/08/01 - Revision 1, Modification 0:

Incorporated calibration requirements per AP-12.1Q; deleted reference to Operating manual; updated instructions and list of NIST standards necessary for calibrating working standard gas for Prism; deleted responsibilities for staff members not directly responsible for implementing this procedure; deleted references to YMP-LBNL-QIPS-12.0, SIII.0, and SIII.3; added reference to AP-SIII.1Q, AP-SIII.3Q and AP-12.1Q, and made minor editorial changes.

10. APPROVAL

Signature on file

Preparer: Mark Conrad — Date

Signature on file

Technical Reviewer: Qinhong (Max) Hu — Date

Signature on file

Technical Reviewer: Eric Sonnenthal — Date

Signature on file

EA Reviewer: Nancy Aden-Gleason — Date

Signature on file

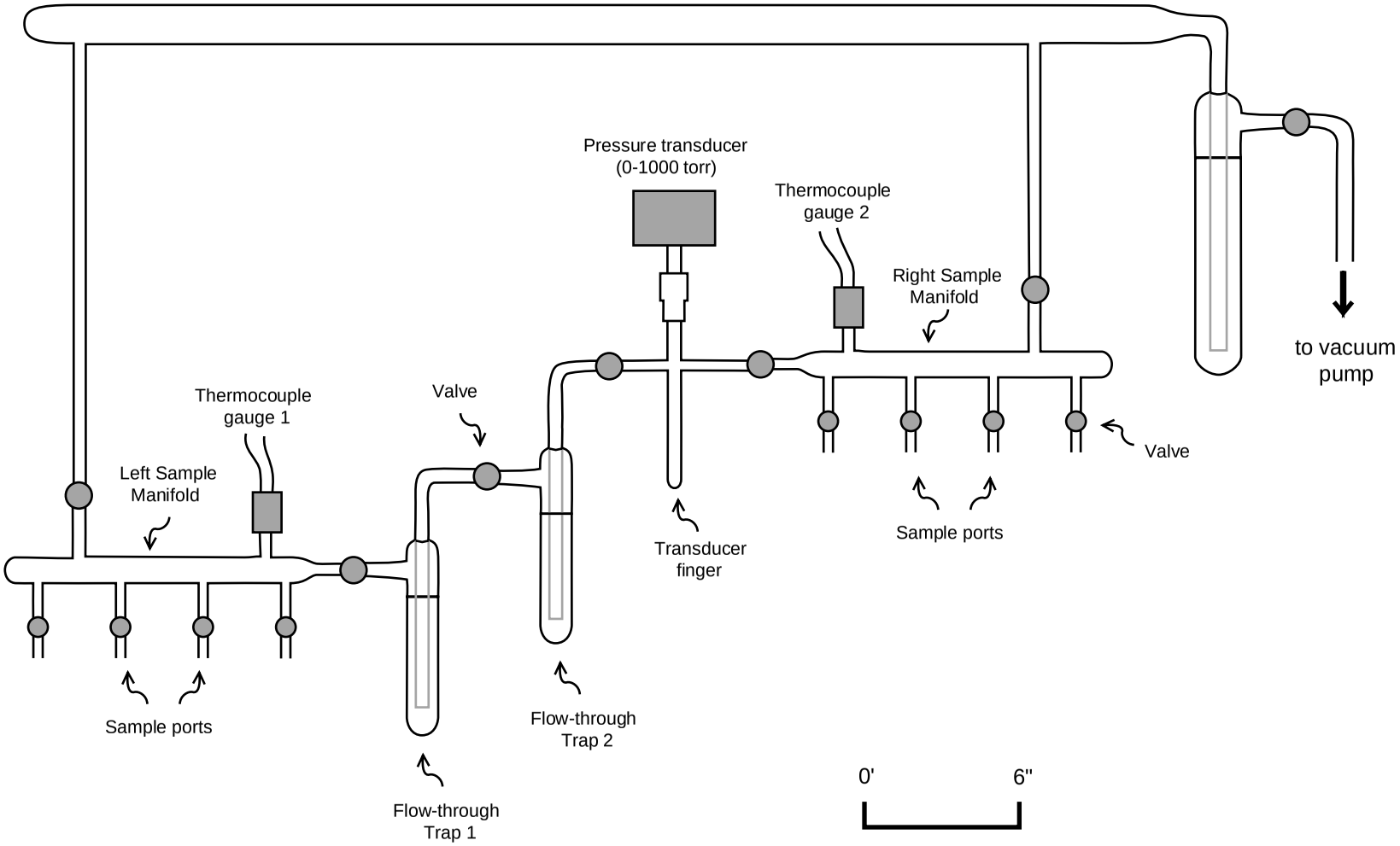
OQA Concurrence: Stephen Harris — Date

Signature on file

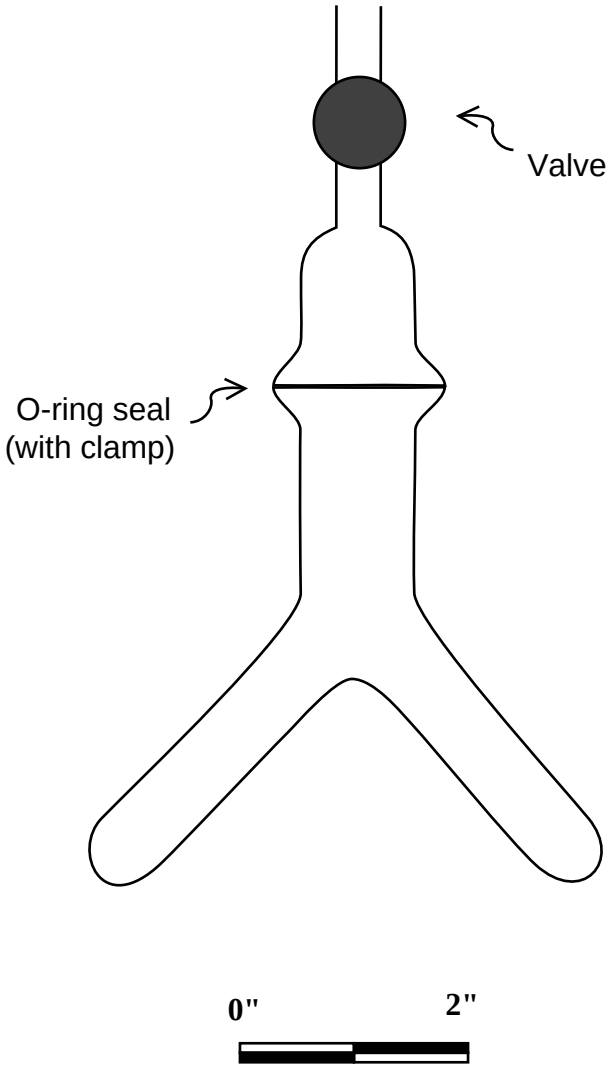
Principal Investigator: Yvonne Tsang — Date

Signature on file

Project Manager: Gudmundur Bodvarsson — Date



Schematic diagram of the vacuum line used for preparation of H_2 and CO_2 for working standards.



Schematic diagram of two-legged reaction vessel used for reacting ortho-phosphoric acid with carbonate materials for isotopic analyses.

M&TE Calibration Documentation Form

<table>
<tr><td>a) M&TE description</td><td>b) M&TE unique identification</td><td>c) Calibration date and time (if applicable)</td></tr>
<tr><td colspan="2">d) Person performing calibrations</td><td>e) M&TE condition (as-found)
Working _____

Not working _____</td></tr>
<tr><td colspan="2">f) Calibration procedure (including revision level)</td><td>g) Calibration standards used</td></tr>
<tr><td colspan="2">h) Location of calibration data

YMP-LBNL-_____
Page(s):</td><td>i) Location of calibration results

YMP-LBNL-_____
Page(s):</td></tr>
<tr><td colspan="3">j) Specified range and tolerances</td></tr>
<tr><td colspan="3">k) Statement of acceptability including acceptability of range and tolerances
Range acceptable Yes _____, No _____
Tolerance acceptable Yes _____, No _____
Calibration acceptable Yes _____, No _____
Comments:</td></tr>
<tr><td colspan="2">l) Re-calibration due date or calibration interval/frequency</td><td>m) Reference to actions taken with out-of-calibration or non conforming M&TE, including evaluation results, as appropriate

YMP-LBNL-_____
Page(s):</td></tr>
<tr><td colspan="3">n) Comments</td></tr>
</table>

Signature Date